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THE MECHANISM OF CHEMISORPTION FROM THE
STANDPOINT OF THE LATTICE VACANCY THEORY

[Comment: This report gives in full the text of a reprint of an article from Zeitschrift fuer Elektrochemie - Berichte der Bunsengesellschaft fuer physikalische Chemie (Journal for Electrochemistry - Reports of the Bunsen Society for Physical Chemistry) Volume 56, No 4, 1952, published in Weinheim. The authors are Karl Hauffe and H. J. Engell, of the Physical-Chemical Institute of the University of Greifswald.

According to the source, the article represents a preliminary discussion of the theory of chemisorption and the electrical conductivity of semiconductors, which is to be detailed shortly by the authors, together with W. Schottky. Reportedly, Engell presented an abbreviated form of this discussion at the Discussions of the Deutsche Forschungsgesellschaft in Berlin on 12 January 1952.

Numbers in parentheses refer to appended bibliography.]

Authors' Abstract

Adsorption on semiconducting oxides at high temperatures takes place with the participation of the electrons of the solid body. Correspondingly, an interrelationship exists between adsorption properties and the electronic structure of the adsorbent. The latter is influenced in turn by the lattice vacancy present in the solid body. It is shown that, by migration of electrons between the adsorbent and the adsorbate, a surface stratum forms according to the concept of Schottky and Mott, and the effect of the space charge developing in this surface stratum on the electrical conductivity and adsorption properties of the semiconductor is both qualitative and, in part, quantitative.

Introduction and Statement of the Problem

It is well-known today that the adsorption processes play a significant role, not only in heterogeneous catalysis, but also with all those reactions where a gas reacts with a solid, as in oxidation-reduction reactions for example. For this reason, it is understandable why the phenomena of adsorption have been studied in a large number of researches. The discovery of the elementary processes has not been successful in most cases, in spite of considerable success, for example, the discovery of the true surface, the heat of adsorption, and the efforts concerning the significance of the activation energy of the rate determining component. The following discussion, will cover only the chemisorption of oxygen on metal oxides, without dealing with the various adsorption processes. This restriction has an obvious reason. To thoroughly understand the adsorption of a gas on a solid body, it must be realized that the impingement of the gas molecules on the surface of the solid body can change not only its electronic state,

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but also the ionic lattice in the surface. Thus, it becomes immediately clear that a deeper insight into the adsorption mechanism is to be expected only if the center of interest of the research is shifted to the solid body. For example, it must be clarified how a transfer of electrons from the adsorbent to the gas and return takes place, and how the transfer of the electrons (and ions), at least in zones of the crystals close to the boundary surface, is to be realized.

Even if this were clear, more knowledge of the structure of real crystals was needed to solve the problem.

It is known today that most ionic and valence crystals have lattice vacancies to a greater or lesser degree; i.e., in these crystals, some ions appear in interstitial positions and unoccupied lattice points, so-called lattice vacancies. Similarly, a certain percentage of electrons are "missing," which necessities dealing with quasi-free electrons and electron vacancies, so-called electron defect positions. It is apparent from experimental and theoretical research (1) that only these unattached ions and electrons can migrate in a crystal. It is immediately understandable, therefore, that these unattached ions and electrons have special significance for the adsorption process. This consideration, develops from the physics of semiconductors. Significant also is the Surface Layer Theory of Crystal Rectifiers developed by Schottky and Sperke (2) and independently by Mott (3) and Davidov (4).

The statement of a Theory of Chemisorption of Oxygen or Oxides requires a combination of the Lattice Vacancy Theory of Oxides and the Surface Layer Theory of Crystal Rectifiers. Thus, the first task will be to show how surface stratum formation comes into the adsorption question. It has been especially useful to include certain considerations of Schottky and Sperke in the present problem.

Chemisorption and Surface Stratum Formation

For simplicity, the following considerations have been applied to an electron excess conducting oxide (e.g., zinc oxide). As a result of a metal excess or oxygen deficiency, which at higher temperatures is a specific function of the oxygen pressure and the temperature, this type of oxide forms quasi-free electrons in the lattice. This condition could be determined quantitatively by means of electrical conductivity measurements (5) as well as by thermoelectric and Hall effect measurements (6).

In a number of publications (6, 7, 8, and 9), it has been shown that the surface layers, rather than the solid base material, are frequently responsible for the conductivity of zinc oxide, as well as of other electron excess conductors. Whether these (poorly conducting) surface strata are formed by distinct concentrations of energy at the surface (10 and 11) or under the influence of adsorbed gas atoms or ions is a moot question. However, in the case of zinc oxide, the second possibility might be experimentally suggested. Moreover, Mott (10) has pointed out that the increased binding strength of the electrons at the absolute surface is counteracted by the effect of polarization of these points of attachment by the bound electrons, so that this type of formation of a surface stratum is questionable at least. The following discussion, therefore,

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will deal only with a surface stratum which develops, e.g., at the oxide/oxygen boundary so that adsorbed oxygen atoms give to the quasi-free electrons a lower energy state (see Figure 1 below).

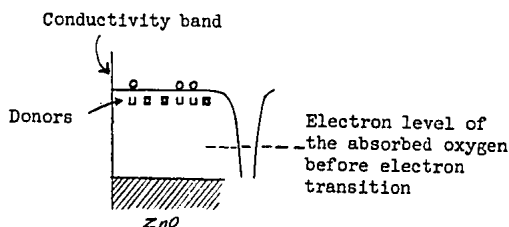
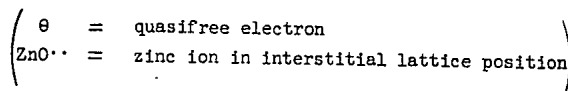
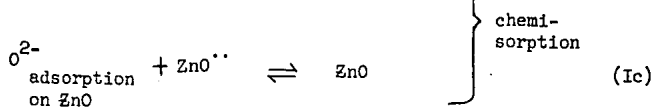
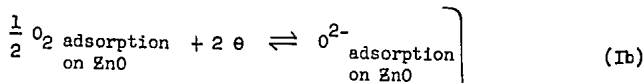
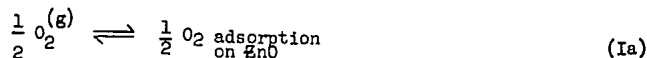


Figure 1

Through the electron affinity of oxygen at not too high temperatures, the flow of electrons takes place only from the zone adjacent to the surface of the semiconductor which we call the surface stratum. The distribution of the electrons in the surface stratum will be defined by the fact that, at each point of the semiconductor in stationary equilibrium, the diffusion stream of electrons in the concentration gradient must be counter both to the field current of electrons under the repelling effect of the surface changes and to the chemisorbed oxygen ions; that means that the oxygen arriving at the surface of the zinc oxide has caused the building up of a space charge layer in the Schottky and Mott concept. This process may be described by the following steps:



Thus equation Ic, as will become apparent in the following discussion, will describe a process linked to the specific chemisorption equation (Ib), which, on the basis of the low mobility of the zinc ions in the interstitial position, needs to be considered only at higher temperatures. For the following treatment of chemisorption, only equation Ib is considered binding; i.e., the discussion considers only the electron migrations from the surface stratum to the oxygen on the surface. A migration of zinc ions into the interstitial position shall be negligible. In the case of the chemisorption equilibrium, i.e., in the stationary electron equilibrium, if the number of electrons arriving on the surface from the

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surface stratum per unit time is equal to the number of the electrons leaving the surface, the local concentration curve of free electrons in the surface stratum can be described by Figure 2a. Here n_H denotes the number of quasi-free electrons in the interior of the semiconductor per cubic centimeter, and ξ the positional coordinates with the reference $\xi = 0$ at the ZnO/O_2 phase boundary.

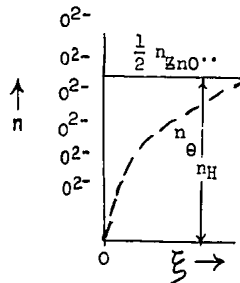


Figure 2a

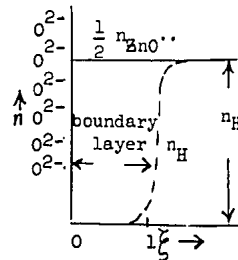


Figure 2b

The corresponding curve of the concentration of the positive interference patterns, in the case of ZnO and the zinc ions in the interstitial positions, will be considerably flatter as a result of the appreciably lower mobility; i.e., in the first approximation it is parallel to the axis. Figure 2b shows an idealized plot of the concentrations which will be used later to calculate the space charges being generated. Here, l mean the thickness of the surface stratum. For simplicity, the appearance of discharge surface strata according to Schottky are considered first. These appear valid at somewhat higher temperatures because, according to Schottky, interference patterns first appear in appreciable number at lower temperatures, and this fact makes the consideration of reserve surface strata necessary.

For excess semiconductors with sufficiently mobile ionic lattice vacancy positions and/or positive interference patterns, a sharply defined surface stratum will be formed, but only from an adsorption origin. The resulting space charge will bring about a transfer of the positive interference patterns to which an enlargement of the surface stratum is connected (see equation 1c). In a stationary condition, the originally sharply defined surface stratum is obliterated and, according to Schottky, has the appearance of a chemical barricade. Concerning this point, Engell, Hauffe and Schottky (12) have reported elsewhere.

In excess conducting mixed oxide phases with higher valence additives (e.g., ZnO with Ga_2O_3), the number of quasi-free electrons can be increased about 2-3 powers of ten, and the number of zinc ions in the interstices are decreased by the same amount, since the majority of the positive interferences pattern is represented by the trivalent cations found in the lattice, e.g. for Ga^{3+} , $\text{Ga} \bullet (\text{Zn})$, which in general have a lower mobility than the cations in the interstices. In accord with the conditions of equilibrium and electrical neutrality

$$n^{\ominus} = n_{\text{Ga} \bullet (\text{Zn})} + 2n_{\text{ZnO}^{\bullet\bullet}} \quad (\text{II})$$

the number of zinc ions in the interstitial positions, which constitute the smallest portion of the positive interference patterns, can be calculated. Similar relationships, however, in inverse concentration distribution, are found in excess conducting mixed oxides with lower valence additives, e.g. $\text{ZnO} + \text{Li}_2\text{O}$. In oxides with electron defect conductivity, such as NiO , FeO , Cu_2O , etc., in contrast to the excess conducting oxides discussed above, in an oxygen atmosphere, a surface stratum with increased conductivity develops so that the conductivity of the polycrystalline

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body is determined by the poorer conducting material of the internal phase. Of course, in this case at high surface stratum conductivity and with high surface stratum thickness relative to the thickness of the crystallite, a form of surface conduction would be conceivable, by means of which the current flows essentially only inside the surface strata (see Figure 3 below). How the surface stratum formation bears on the electrical properties of electron defect conductors will be discussed in a later work (12).

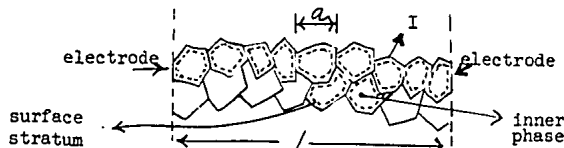


Figure 3

Because the change of the electrical properties in the surface stratum of the ZnO is caused by the change in concentration of the quasi-free electrons and is proportional in return to the number of chemisorbed oxygen atoms, a clarification of the electronic processes in the surface stratum must first be made.

The Mechanism of Surface Stratum Formation During Chemisorption

In the following discussions, the definition of Schottky and Spenke will be used. In accord with these authors, it is assumed that, through the flowing off of quasi-free electrons with the retention of the positive interference patterns in a surface stratum of thickness (see Figure 2b above), a space charge of density ρ forms, which will be set up within the surface stratum as a constant:

$$\rho = e \cdot n_H \quad \text{for } 0 < \xi < l. \quad (\text{III})$$

Here e signifies the elemental charge. On the other side of the surface stratum, the density of the space charge equals 0:

$$\rho = 0 \quad \text{for } l < \xi < \infty. \quad (\text{IV})$$

V_D is denoted the diffusion potential which is regulated between the surface and the interior of the semiconductor; thus it follows from the Poisson function $V''(\xi) = \frac{4\pi}{\epsilon} e \cdot n_H$ (ϵ = dielectric constant):

$$V_D = \frac{2\pi e n_H}{\epsilon} l^2. \quad (\text{V})$$

Because with ZnO the positive excess charge in the surface stratum must be equal to twice the number of attached oxygen ions l may be eliminated from equation V and

$$V_D = \frac{2\pi e \cdot n^2}{\epsilon \cdot n_H} \quad \text{with } n = 2n_{O^{2-}}^{(\sigma)}, \quad (\text{VI})$$

whereby the index σ indicates the adsorption layer or areal phase is obtained.

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Without doubt this equation is meaningful only when

$$F \cdot \ell < v \quad (\text{VII})$$

(F = the surface in cm^2 per mol and V = volume of a mol of the solid ZnO in cm^3), i.e., if the surface stratum volume is appreciably smaller than the total volume of the semiconductor. Since ℓ is related to n_H by

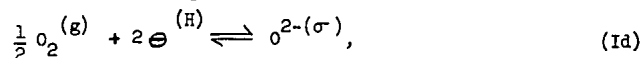
$$\ell = \sqrt{\frac{\epsilon \cdot V_D}{2 \cdot \epsilon \cdot n_H}} \quad (\text{VIII})$$

the above-mentioned condition will no longer be filled for low values of n_H because in this case ℓ becomes too large. This case is to be expected, for example, in electron excess conducting mixed phases where n_H , which here is to be set equal to the number of quasi-free electrons per cubic centimeter, is very small (13). Here the surface stratum at low temperatures is already so indistinct that, to an adequate approximation, the validity of the classic semiconductor theory ("Homogeneous Semiconductor Theory") can be counted on. Also, with too large formation of surface in accord with equation VII, the occurrence of a surface stratum in the true sense is not to be reckoned with. On the other hand, the adsorption as well as the electrical and photoelectrical properties of excess semiconductors which fulfill the condition

$$\frac{v}{F} > \sqrt{\frac{\epsilon \cdot V_D}{2 \pi \epsilon \cdot n_H}} \quad (\text{IX})$$

will be definite in the case of the formation of this surface stratum.

In accord with the reaction equation



where the index (H) denotes a particle in the semiconductor and the index (σ) denotes a particle at the surface, the chemisorption equilibrium exists if the sum of all the electrical potentials η is

$$\sum v_i \eta_i = 0$$

or, by use of the in eV calculated chemical and electrical potentials μ and V , if

$$\frac{1}{2} \mu_{\text{O}_2}^{(g)} + 2 \mu_{\Theta}^{(H)} - \mu_{\text{O}^{2-}}^{(\sigma)} + 2 (V^{(\sigma)} - V^{(H)}) = 0. \quad (\text{X})$$

As shown by Engell, Hauffe, and Schottky (12), elsewhere, equation X translates into

$$\frac{1}{2} \mu_{\text{O}_2}^{(g)} + 2 \mu_{\Theta}^{(H)} - \mu_{\text{O}^{2-}}^{(\sigma)} + 2 V_D = 0. \quad (\text{Xa})$$

The Influence of the Surface Stratum Formation on the Conductivity of Polycrystalline Oxide Semiconductors

To understand the value of the Surface Stratum Theory for the development of a theory of chemisorption on oxide electron excess conductors, we must first deal with the electrical conductivity in the surface stratum and the oxygen pressure dependence of the conductivity. As will be shown in the course of the work, the physicists and chemists who study semiconductors have made contributions to the clarification of chemisorption.

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1. General Calculation of the Conductivity of the Surface Stratum

The electrical conductivity of the surface stratum formed by the surface binding (chemisorption) of oxygen may be approximated from the formulas derived in equations III through Xa.

With the assumption that the distribution of the quasi-free electrons in the semiconductor, including the surface, is in accord with Boltzmann statistics, the relationship of the internal phase and surface stratum concentration of quasi-free electrons is given by the formula

$$\frac{n_R}{n_H} = \exp. (-v_D/\beta) \quad (XI)$$

in which $\frac{kT}{e} = \beta$ is used. With $n_R / n_H = \kappa_R / \kappa_H$, the resistance effective at right angles to the lateral face of a surface stratum W_R is found from the general statement:

$$W_R = \frac{1}{q} \int_0^L \frac{1_d E}{\kappa} \quad (XII)$$

Furthermore, if a is the average edge length of a crystallite, there are, in a canal of length L (tablet length, see Figure 3 above), $2L/a$ surface strata to pass through. If the resistance of the surface strata is several powers of ten higher than the internal phase, the internal phase resistances can be neglected; and by considering $\kappa_H = \text{constant} \cdot n_H$ for the "apparent specific conductivity" $\kappa_{\text{eff.}}$ of the tablet, the expression

$$\kappa_{\text{eff.}} = \text{const} \cdot a \cdot n_H^{\frac{3}{4}} \cdot v_D^{\frac{1}{2}} \exp(-v_D/\beta) \quad (XIII)$$

is obtained. Equation XII reproduces the conductivity of the surface stratum κ_R and, in the case $\kappa_H \gg \kappa_R$, the apparent specific conductivity of the sintered body and/or polycrystalline semiconductor is also given. $\kappa_{\text{eff.}}$ is, therefore, proportional to the lattice vacancy concentration present in the internal phase. The temperature dependence of the conductivity will be given principally by the exponential term as well as by the temperature dependence of n_H as will be shown later. Equation XIII describes accordingly the actual conductivity formula of an electron excess conducting sintered oxide with poor surface stratum formation.

2. Calculation of the Oxygen Pressure Dependence at the Conductivity of the Surface Stratum

In stationary equilibrium the number of the oxygen ions being chemisorbed per unit time will be equal to the number of oxygen ions being desorbed per unit time. According to equation Ib,

$$\frac{d}{dt} n_{O_2}^{(\sigma)} = 0 = k_a \cdot n_R^2 \cdot p_{O_2}^{\frac{1}{2}} - k_d n_{O_2}^{(\sigma)} \quad (XIV)$$

is obtained. Using equation XI, it follows that

$$n_{O_2}^{(\sigma)} = \frac{k_a}{k_d} \cdot n_H^2 \cdot p_{O_2}^{\frac{1}{2}} \cdot \exp(-2v_D/\beta) \quad (XV)$$

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Considering the relationships derivable from the Poisson function for the field strength of the surface stratum,

$$\mathcal{E} \sim N_D^{\frac{1}{2}} V_D^{\frac{1}{2}} \quad (N_D = n_H) \quad (\text{XVI})$$

and

$$\mathcal{E} = \frac{4\pi e}{\epsilon} \cdot 2n_{O_2}^{(\sigma)} \quad (\text{XVII})$$

it follows from equation XV that

$$V_D \left(\frac{k_a}{k_o} \right)^{\frac{2}{3}} \frac{n_H^{\frac{4}{3}} \cdot p_{O_2}}{N_D} \exp. (-4 V_D / 23). \quad (\text{XVIII})$$

If the interference pattern density in the semiconductor n_H is set as equal to the total density of the donors in the internal phase of the semiconductor N_D , which is possible for the case of a discharged surface stratum, then by applying logarithms and rearranging

$$\frac{V_D}{23} = \ln (K \cdot N_D^{\frac{3}{4}} \cdot p_{O_2}^{\frac{1}{4}}) - \ln V_D^{\frac{1}{4}}. \quad (\text{XIX})$$

results. From this expression, there is found for the electrical resistance in the surface stratum W_R ; then from the Engell, Hauffe and Schottky (12) expression,

$$\ln W_R = \text{const} + \ln p_{O_2}^{\frac{1}{4}} - \ln N_D^{\frac{3}{4}}, \quad (\text{XX})$$

i.e., for the electrical conductivity,

$$\kappa_{\text{eff.}} = \text{const.} \cdot N_D^{\frac{3}{4}} \cdot p_{O_2}^{-\frac{1}{4}}. \quad (\text{XXI})$$

is valid. This expression makes it understandable why, at relatively low temperatures (below 300°C), the regulation of the electrical conductivity, with the oxygen pressure takes place relatively quickly and that $\kappa \sim p_{O_2}^{-\frac{1}{4}}$.

In such cases, predominant surface stratum conductivities are probably being dealt with.

Equations XIII and XXI can be utilized with greater validity only if the resistance of the surface stratum is significantly higher than that of the internal phase. The other possibility for strict validity of equation XXI would be for a crystallite size of the same order of magnitude as λ . Whether it is generally justifiable to accept the simplifications of the Schottky Surface Stratum Theory appears doubtful.

3. Calculation of the Oxygen Pressure Dependence of the Conductivity of Polycrystalline Sintered Bodies of an Electron Excess Conductor Assuming Comparable Resistances of the Surface Stratum and the Internal Phase.

Great differences in the conductivity values of the surface stratum and the internal phase are to be expected especially at low temperatures because the mobility of the positive interference patterns in the presence of electrical fields is very slight at these temperatures and, for another reason, the exponential term in equation XI becomes larger with decreasing temperature. These are, however, two important premises for the formation of surface strata. At very high temperatures, as

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discussed above, there is no formation of a discrete surface stratum. Through an estimation, it can be shown that the enlargement will, in general, be small (14).

The conductivity is now considered under the following conditions:

- a. Equal conductivity in the surface stratum and the internal phase at p_{O_2} approaching 0 ($v_D \rightarrow 0$).
- b. Change in the resistance of the surface stratum according to equation XXI.

Then

$$\frac{1}{K} = \frac{a - 2l}{a} \cdot \frac{1}{K_H} + \frac{2}{a} \cdot W_R ;$$

therefore, according to equation XXI

$$\frac{1}{K} = \left(1 - \frac{2l}{a}\right) \frac{1}{K_H} + \frac{2C}{a} \cdot p_{O_2}^{1/4} , \quad (XXII)$$

whereby, according to equation XX C is proportional to $N_D^{-3/4}$.

After rearrangement,

$$K = K_H \frac{\alpha}{\alpha + p_{O_2}^{1/4}} , \quad (XXII)$$

with

$$\alpha = \left(1 - \frac{2l}{a}\right) \frac{a}{2CK_H} .$$

From this, for the case of $\alpha \ll p_{O_2}^{1/4}$, it follows that

$$K \sim p_{O_2}^{-1/4} .$$

The oxygen pressure dependence of the conductivity decreases with increasing value of α according to equation XXII. Because

$$\alpha \sim N_D^{3/4} ,$$

the influence of the oxygen pressure on the conductivity must decrease accordingly with increasing N_D . The experimental proof for this may be shown by measurement of the oxygen pressure dependence of the conductivity of ZnO mixed oxides in which N_D

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is varied (see Figure 4 below). Furthermore, it is possible to determine the relationship of the surface stratum thickness to the size of the crystallite from equation XXIII.

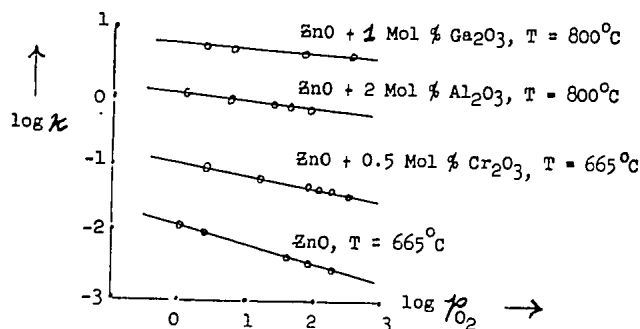


Figure 4

If the crystallite size a can be determined from other measurements (e.g., determination of the surface area and the apparent specific density), V_D may be calculated from κ . This value was estimated on the basis of the theoretical considerations of Mott to be about 2 to 3 volts. It would be interesting to establish whether V_D actually has this relatively high value.

As a second approach, the oxygen pressure dependence of κ might be considered; however, this appears to be within the limits of accuracy of the measurement and of slight value at present. The assumptions made in this paragraph (χ_R comparable with χ_H) were confirmed by Miller (7) for ZnO at room temperature.

The Chemisorption Isotherm on Electron Excess Conducting Oxides

After these preliminary observations, the establishment of the adsorption isotherm will now be considered. From equation VI, the amount of oxygen adsorbed on an excess conductor for constant oxygen pressure may be calculated as follows:

$$n_{O_2}^{(\sigma)} = \frac{1}{2} n_{\sigma} = \frac{1}{2} \sqrt{V_D \cdot \frac{\epsilon \cdot n_H}{2 \pi e}} \quad (XXIV)$$

In two otherwise similar semiconductors, the adsorbed oxygen is proportional to the square root of the concentration of lattice vacancies. In fact, V_D is also dependent on n_H ; however, this (logarithmic) dependence may be negligible.

The equation of the specific adsorption isotherm ($n_{O_2}^{(\sigma)} = f(p_{O_2})$, $T = \text{const}$) is given from equation XV. The exponential term is eliminated by means of equation XIX and

$$n_{O_2}^{(\sigma)} = \frac{1}{4} \frac{\epsilon}{\pi e} \cdot N_D \cdot \ln \left[\frac{p_{O_2}^{1/2} \cdot n_H^2 K}{n_{O_2}^{(\sigma)}} \right]^{1/2} \quad (XXV)$$

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is obtained. The surface concentration $n_{O_2}(\sigma)$ of oxygen increases with the logarithm of the oxygen pressure. This form of an isotherm can be held as characteristic for a chemisorption in which a space charge is formed on the surface of the solid.

Oxygen Pressure Dependence of the Conductivity on ZnO and of ZnO With Higher Valence Additives

From analysis of the measurements of the oxygen pressure dependence of the conductivity of ZnO and ZnO with higher valence additives (15 and 16), contradictions can very definitely be shown by referring to the concomitant change in conductivity with change of oxygen pressure by a change in the concentration of quasi-free electrons throughout the semiconductor. From the conductivity-oxygen pressure curve, the amount of gas adsorbed may be calculated between the oxygen pressure limits of $p_1 = 0.1$ to $p_2 = 10^3$ mm Hg. For pure ZnO at 665° , the value of about 3.5×10^{-4} mol of oxygen per mol of zinc oxide is obtained, which is equivalent to 7.5 cubic centimeters of oxygen at normal temperature and pressure. For a mixed phase with 1 mol % of Ga_2O_3 at $800^\circ C$, from the conductivity according to Hauffe and Block (16) for the same pressure change, there is found to be about 0.12 mol of oxygen per mol of ZnO, or about 2.7 liters of oxygen at normal temperature and pressure. That this amount is absurdly high, will be clearer from the following observation:

Assuming an average edge length of 10^{-5} cm for the cubic crystallite which had been sintered for 4 hours at $1100^\circ C$, there is an area of 10^7 square centimeters per mol. (Actually the surface area might be about one power of ten smaller, or about one square meter per gram of ZnO). Assuming further that each oxygen atom covers an area of $10 \text{ \AA}^2 = 10^{-15}$ square centimeters, then the amount of oxygen calculated above would cover an area of 4×10^5 square centimeters with pure ZnO. The surface would be about 4% covered with oxygen. In the case of $ZnO.Ga_2O_3$ mixed crystal, on the other hand, there would have to be seven to eight layers of oxygen atoms on top of one another! That is, of course, completely impossible at 800° . If it is assumed, on the other hand, that only within a surface stratum, the thickness of which is small compared to the edge length of the crystallite, the concentration of the quasi-free electrons is changed, then this inconsistency is removed. Experimentation to verify the derived interrelationships is in progress and will be published soon.

In a publication soon to appear, written together with Prof Dr W. Schottky (12), the concepts developed briefly above are expanded and defined and it will be shown that their application to a series of phenomena -- above all, chemisorption and its importance to the catalytic properties of semiconductors -- leads to new and interesting conclusions.

The authors are indebted to Prof Dr W. Schottky for stimulating and critical discussion, as well as for his interest in the formulation of their reasoning.

DISCUSSION

W. Meyer, Berlin: From the discussion of the lecturer, it must be inferred that the conductivity κ of the ZnO depends greatly on the grain size of the sintered body. On the other hand, it is indicated that the electrical behavior of monocrystalline, compact-grained, and coarse-grained ZnO does not differ from one another. Such an inference, in my opinion, is invalid, not only for the oxygen pressure dependence of κ , but also for the known relationship between κ

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and the total internal work function ϵ . Also, with other oxide semiconductors, no difference would be established between monocrystalline and compact-grained structure with respect to the electrical behavior.

Answer: The comments of Dr Mayer are well taken because, for the electrical conductivity, there are two possibilities:

1. The previous measurements on zinc oxide are apparently for sintered material which consists of a very small crystallite, so that the average crystallite thickness a was almost equal to the surface stratum thickness l .
2. The crystallites are so large that the resistance of the internal phase is appreciably larger than the total of all surface strata; thus, the influence of the surface stratum resistances on the total conductivity is negligible. This case occurs when α is very large and K_H is not significantly larger than K_R .

The opinion expressed by Dr Meyer concerning the monocrystalline and polycrystalline materials, we cannot share. According to Bevan and Anderson (Disc. Faraday Soc. No 8, 238 (1950)), the temperature dependence of the conductivity of ZnO monocrystals in air, according to the measurements of Fritsch, correspond to those of polycrystalline ZnO in a vacuum. Furthermore, the dependency on frequency of the conductivity of ZnO according to Miller (Semi-conducting Materials, page 172) may be cited in this connection.

E. Cremer, Innsbruck: To clarify the course of the measured adsorption isotherm, we use the equation $\ell = (\ell_m - \ell_0)(1 - \sigma) + \ell_0$, which means that the energy of adsorption (ℓ) from ℓ_m to ℓ_0 decreases linearly with increasing degree of coating σ . We have tried to explain this statement by the fact that, for the first adsorbed molecule, more electrons are available than for those molecules which are absorbed later. The precise formulation of this state of affairs appears to me to have been given by the calculations of Aigrain and Dugas, as well as by those of Haufler and Engell for certain cases.

Answer: Of course, the dependency of the heat of adsorption might be explained by the scale thickness from our suggestions. By the flow of electrons out of the surface stratum of the semiconductor, the energy distribution of the electrons in the semiconductor is disturbed; and, for the maintenance of this distribution, the solid body must absorb energy Q , which is obtained from the heat of adsorption Q and, therefore, is to be subtracted from it as follows:

$$Q^{\text{eff.}} = Q - \Delta Q$$

$$\Delta Q = f(n_\sigma)$$

where n_σ is defined by the surface concentration of the adsorbate.

G. -M. Schwab, Munich: The difference between ours and the Haufler concept, which represent both extremes, lies in that we consider it possible that, at the center of disturbance, conditions prevail other than those in the intact neighboring surface; while, with Haufler's representation, the role of the disturbance center disappears in the control of the electron intake and outgo. The experiment will have to decide in each particular case between these possible extremes.

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Answer: The decision lies with the surface phenomena, e.g. chemisorption; the concentration of the electron disturbance centers on the surface. The ionic disturbance centers have only an indirect duty, i.e., to determine the absolute value of the ionic and electronic lattice vacancy concentration before the adsorption, since both are coupled on the basis of the condition of electrical neutrality. Obviously, the ionic disturbance centers in the form of the Schottky surface stratum (width, etc.) have a significant influence which follows from our exposition.

E. Krantz, Braunschweig: The statement that, in the zinc oxide excess semiconductor, the excess zinc is assumed to be localized in the interstitial positions must be considered quite improbable, in view of the most recent findings concerning the location of foreign atoms both with semiconductors and also with crystalline phosphors. The fact that the foreign atoms become migratory at high temperatures is proof that the foreign atoms undergo the same lattice position change as the normal lattice atoms. From the process of excess conduction with zinc oxide, it is true that the lattice vacancy arises from the formation of oxygen deficiency points and not from the introduction of zinc in the interstices of an ideal lattice.

Answer: The recent information cited by Dr Krantz concerning the introduction and migration mechanism of foreign atoms in ZnO is not known to us and appears to us hardly plausible in view of the experimental findings to date.

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